91602
new 82-10

COMPLIMENTARY COPY
Please Credit Ontario Hydro Research if
Reproduced in Whole or in Part

LEGAL NOTICE

This report was prepared by Ontario Hydro and, while effort has been made to assure the accuracy and applicability of the material contained herein, neither Ontario Hydro nor any person acting on its behalf:

(a) makes any warranty, express or implied with respect to the use of any information, apparatus, method or process disclosed in this report or that such use may not infringe privately owned rights; or

(b) assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method or process disclosed in this report.

ontario hydro
research division

CORROSION AND TRITIUM TECHNOLOGY SECTION 1990 REVIEW AND 1991 WORK PROGRAM

Report No. 91-99-K

P.C. Lichtenberger, Supervising Scientist
Corrosion & Tritium Technology Section
Metallurgical Research Department

ABSTRACT

The key projects and achievements of the Corrosion and Tritium Technology Section (C&TT) during 1990 are reviewed and the work program for 1991 is highlighted. The section activities continue to be concentrated in the areas of Zr alloy corrosion/hydrogen ingress mechanisms, steam generators/heat exchanger corrosion mechanisms, tritium handling/storage processes, and tritium interactions with metals.

job	file	date	report no.
	100	May 7, 1991	91-99-K

TABLE OF CONTENTS

		PAGE
1.	INTRODUCTION	1
2.	RESEARCH AND DEVELOPMENT PROGRAM OVERVIEW	1
	2.1 Corrosion	1
	2.2 Tritium Technology	2
	2.3 Funding/Clients/Staffing	3
3.	CORROSION PROGRAM	4
	3.1 Pressure Tube Corrosion and Deuterium Ingress	4
	3.1.1 Pressure Tube Corrosion and Deuterium Uptake in Reactor Pressure Tubes	4
	3.1.2 Exposure Testing	5
	3.1.3 Mechanism of Deuterium Ingress	7
	3.1.3.1 Deuterium Concentration Profiles	7
	3.1.3.2 Oxide Structure	8
	3.2 Heat Exchanger Corrosion	9
	3.2.1 Program Background	9
	3.2.2 Field Studies	9
	3.2.3 Laboratory Studies	10
	3.2.4 1991 Plans	10
	3.2.4.1 Mechanism Determination	10
	3.2.4.2 Life Predictions	11
	3.2.4.3 Mitigation	11
	3.2.4.4 Monitoring	11
	3.3 Corrosion Engineering	11
	3.4 Steam Generator Tubing Corrosion	12
	3.4.1 Corrosion Fatigue	12
	3.4.1.1 1990 Review of Progress	13
	3.4.1.2 1991 Plans	13
	3.4.2 Stress Corrosion Cracking	14
	3.4.2.1 1990 Review of Progress	14
	3.4.2.2 1991 Plans	14

TABLE OF CONTENTS (CONT'D)

			PAGE
3.4.3	Steam Generator Corrosion Surveillance		15
3.4.3.1	1991 Review of Progress		15
3.4.3.2	1991 Plans		15
4.	TRITIUM TECHNOLOGY PROGRAM		16
4.1	Program Objectives		16
4.2	1990 Program Review		16
4.2.1	Metal Getter Program		16
4.2.1.1	ZrCo Beds		16
4.2.1.2	Consulting		16
4.2.1.3	Uranium Particulate Control		16
4.2.1.4	Consequence of Air Ingress into Uranium Storage Bed		17
4.2.1.5	Scavenger Bed Development		17
4.2.1.6	Filter Plugging		17
4.2.2	Tritium/Metal Interaction Studies		17
4.2.2.1	Permeation		18
4.2.2.2	Decontamination		19
4.2.2.3	Tritium Powered Lights		19
4.2.3	Gas Handling/Equipment Development		20
4.3	1991 Research Plans		20
4.3.1	Research Program in Support of DNGS		20
4.3.1.1	Development of a Decontamination Center		20
4.3.1.2	Improvements to the Assay System of TIS		21
4.3.1.3	Consulting in Support of the TRF Annex		21
4.3.1.4	Turbomolecular Pump Decontamination and Balancing		21

TABLE OF CONTENTS (CONT'D)

		PAGE
4.3.2	Tritium Interaction with Metals	21
4.3.2.1	Decontamination	21
4.3.2.2	Low Water Retention Surfaces	22
4.3.3	Tritium Laboratory Support Programs	22
4.3.3.1	Computerized Data Acquisition System	22
4.3.3.2	SEC System Development	24
4.3.4	Metal Getter Studies	24
4.3.4.1	Scavenger Evaluation Program	24
4.3.4.2	Aging Effects of ZrCo and ST737	24
5. ACKNOWLEDGMENTS		25

TABLE

		PAGE
Table 1	Corrosion and Tritium Technology Staff as of Year End 1990	26

FIGURES

		PAGE
Figure 1	Deuterium Contents from all Removed/ Scraped Pressure Tubes	5
Figure 2	Deuterium vs Oxygen Weight Gain for Zr-2.5 wt% Nb Samples (static autoclave, 500 days, aqueous D_2O, pH 10.5, 310°C)	6
Figure 3	Through Thickness Deuterium Concentration Profiles in Outside Surface Oxides from Outlet of B1L08	7
Figure 4	Schematic of Typical Oxide Microstructure on Zr-2.5 wt% Nb As-Received Pressure Tube	8
Figure 5	Cross-section of 5 kg Uranium Scavenger Bed	18
Figure 6	Tritium Released from Stainless Steel (Sample #3)	23

ontario hydro
research division

To Dr. D. Mills
Director of Research

CORROSION AND TRITIUM TECHNOLOGY SECTION
1990 REVIEW AND 1991 WORK PROGRAM

1. INTRODUCTION

This report presents an overview of the C&TT Section work programs, the key progress achieved during 1990, and the direction in which the work program will be focused in 1991.

The mission of the section continues to be to carry out R&D, perform technical investigations and act as a corporate centre for expertise in the areas of metallic corrosion mechanisms/control, and tritium-metal interactions/tritium handling. The section is accordingly divided into two main work groups - Corrosion (60%) and Tritium Technology (40%).

2. RESEARCH AND DEVELOPMENT PROGRAM OVERVIEW

2.1 Corrosion

Pressure tube Zr alloy corrosion and hydrogen ingress mechanisms work remains high priority accounting for 25% of the section's efforts. The critical need is to understand these processes so that reliable predictions of current pressure tube life can be made, and also so that improved materials and/or operating procedures can be established to extend the life of these components. Research is concentrated on heat transport system coolant effects, alloy microchemical/microstructural effects, and annulus gas effects. The critical hydrogen ingress process is controlled by permeation through the normally protective surface oxide present on the tubes. Characterizing and defining the oxide formation and degradation mechanisms on a microscopic level is seen as the route to understanding and predicting such permation.

Nuclear Steam Generator tubing corrosion mechanism research also continues to be a key activity accounting for 17% of the section's efforts. Despite an overall very good record of performance reliability, there continues to be increasing concern as to the long term integrity of alloy 600 tubing. Anticipatory research is being conducted in the areas of stress corrosion cracking, corrosion fatigue, and under deposit localized corrosion degradation. Generic degradation of this kind has led to large incapability in nuclear steam generating equipment around the world. Deposit build-up in Bruce 'A' generators caused additional deratings in 1990 due to flow blockage at tube support plates. At Bruce 'B', fretting wear at 'U-bend' supports, has

been identified from extensive surveillance examinations as a potentially serious generic degradation mechanism where flat bar AVB's are in use. Darlington Steam Generators employ a flat bar support structure as well. Under both of these conditions, there is an increasing risk of corrosion related degradation to the tubing.

A substantial research effort continues to quantify under-deposit pitting and other local corrosion degradation mechanisms associated with nuclear plant heat exchangers. This work now accounts for roughly 12% of section activity. Work remains focused on establishing the role of alloy chemistry and microchemistry, microbiology, and deposit formation. Electrochemical techniques and high sensitivity surface analysis methods combined with laboratory and site exposure test rigs, continue to form the basis of these activities. A major increased effort in 1990, which will continue through 1991, is associated with the potential synergistic role of Zebra Mussels in the corrosion process.

The remaining 6% of activities in the corrosion program involves corrosion engineering support to nuclear, thermal, and hydraulic plant equipment, as well as transmission, distribution and other related equipment. The main efforts remain directed toward corrosion failure evaluation and analysis, corrosion control methods, corrosion monitoring, and selection/evaluation of materials to reduce or eliminate corrosion. In the last year these activities have increased. This application of expert corrosion advice and testing provides large cost benefit ratios, often exceeding a factor of 10 or more. During 1991 continuing activity is expected to address corrosion implications of rapidly accelerating Zebra Mussel infestations in the Great Lakes, increased S/G tubing surveillance examinations and the implementation of electrochemical monitoring technology.

2.2 Tritium Technology

Tritium Technology R&D is primarily focused on supporting a number of corporate groups and activities directly associated with the handling and exposure to tritium and tritium contamination. A main continuing component of this work involves metal getter research and development, which accounts for 10% of the section work activity. Getters are an extremely safe and effective way of storing and immobilizing large volumes of hydrogen isotopes. This work directly supports Darlington TRF and the day to day operation of the Research Division Tritium Laboratory. Activities involve characterization/ quantification of getter properties and kinetics and the testing of improved getter alloys. This work has also led to the design and development of practical and efficient storage and recovery devices/systems which are being commercially marketed by the Canadian Fusion Fuels Technology Program (CFFTP).

The study of tritium interactions with materials, has increased to 15% of section effort. Hydrogen isotopes due to their small atomic volume and mass, are easily adsorbed/absorbed and rapidly permeate most engineering materials. Add to this the emission of an energetic beta particle (resulting from the decay of the tritium atom) and there exists the potential for progressive material property degradation. Understanding these processes is crucial to

understanding tritium effects in fission and potential fusion material processes. Both applied and basic work continues to investigate the nature and consequences of material degradation, unique gas separation/filtering methods, decontamination, and advanced "Tritium Light" concepts/devices.

In order to study tritium materials interactions, gas handling systems/processes are required. The development of these facilities accounts for the final 15% of the section work program. A divisional tritium laboratory continues in operation. Operation/development of this lab facility is providing invaluable knowledge/experience in the development and application of tritium monitoring, tritium control and cleanup of work environments, specific tritium handling practice and tritium materials compatibility. Support in commissioning and operating the tritium immobilization system of the Darlington Tritium Removal Plant and the design/construction of a tritium dispensing loop (TAP) is a direct application of the tritium lab operational experience.

2.3 Funding/Clients/Staffing

In 1990, the 3.7M$ work program of the C&TT section was roughly 70% transfer funded. By far the bulk of the work continues to be in the Nuclear Generation program area with principal clients being Technical and Training Services Division, Nuclear Generation Division, and Design and Development Division. Work performed on behalf of the CANDU Owners Group (COG), accounted for 80% of all corrosion related transfer funds and for 1991 this will continue. This large proportion of committed work continues to have a major impact in terms of our ability to respond to short term corrosion work requests from other clients. The current volume of requested corrosion R&D work remains fully at the limit of available staff resources to undertake the work. If anticipated increases in 1991 in corrosion work to continue to fully support S/G tube surveillance and Zebra Mussel programs are realized, we may be forced to delay or drop some other committed priority work. Transfer funding of the Tritium Technology program accounts for about 60% of the total program costs. Four main client groups, the Canadian Fusion Fuels Technology Program (CFFTP), New Business Ventures Division (NBV), the Darlington Project, and the National Fusion Program, continue to share the total effort.

The staff of the Corrosion and Tritium Technology Section are listed in Table 1. During 1990, a number of additional researchers were temporarily attached to the Tritium Technology Group: one from CFFTP, a University of Toronto Masters Student, a scientist from the Idaho Nuclear Engineering Laboratory, a technician and Engineer from Princeton TFTR, and a visiting scientist from Italy (CNEA). On the corrosion side, an AECL scientist spent 50% of his time at our labs.

Internal reports and external publications/presentations, visits and visitors are also attached.

The following sections provide highlights of the key activities of the work program in terms of significant 1990 progress and planned objectives for 1991.

3. CORROSION PROGRAM

3.1 Pressure Tube Corrosion and Deuterium Ingress

3.1.1 **Modelling Corrosion and Deuterium Uptake in Reactor Pressure Tubes**. The objectives of this program are to collate and analyze data from research programs and from removed reactor pressure tubes on corrosion and deuterium uptake in zirconium alloys. Benefits include providing a central source of data on pressure tubes with analysis and predictions of pressure tube performance for OH design and operations groups.

Recent data from Pickering 3 and 4, and Bruce 1 have been included in the data base and analyzed. To date, most deuterium concentration measurements and all corrosion oxide thicknesses in operating Zr-2.5 wt% Nb pressure tubes appear to be gradually increasing with reactor operating time. This is shown in Figure 1 (area under the dashed line) for all removed/scraped pressure tubes in terms of deuterium pickup. Deuterium uptake rates appear to be constant and <2 ppm year in this region and appear to be associated entirely with the inside surface corrosion reaction.

There are some tubes exclusively from Pickering 3 and 4 with higher levels of deuterium (above dashed line in Figure 1). Their peripheral or clustered lattice locations suggest the influence of operational variables which we believe are associated with annulus gas operation. This evidence combined with the overall higher ingress rates of pressure tubes at Pickering compared to Bruce A, and the previously poorly oxidizing annulus gas environment at Pickering, suggests a significant contribution of deuterium arising from the annulus gas in selected Pickering pressure tubes. Recent additions of O_2 to Pickering 4 (~0.5 wt%), and the expected higher oxidizing potential of the CO_2 annulus gas at Bruce A, together with planned oxygen addition, should provide an environment in which the above annulus gas mechanism is unlikely to contribute appreciable ingress of deuterium, provided O_2 can access the pressure tubes (eg, no absolute blockage).

Zr-2.5 wt% Nb pressure tubes show both increasing corrosion and deuterium ingress from inlet to outlet regions. Oxidation rates are generally slightly higher at Bruce A compared to Pickering A as expected from the higher operating temperatures, although average deuterium ingress rates are slightly lower. Deuterium concentrations generally follow inside surface oxide thickness (corrosion). Inside surface oxides are generally thicker as expected at the hotter 6 o'clock location. Deuterium concentrations are higher at the colder 12 o'clock location probably as a result of thermal migration in this exothermic occluding material.

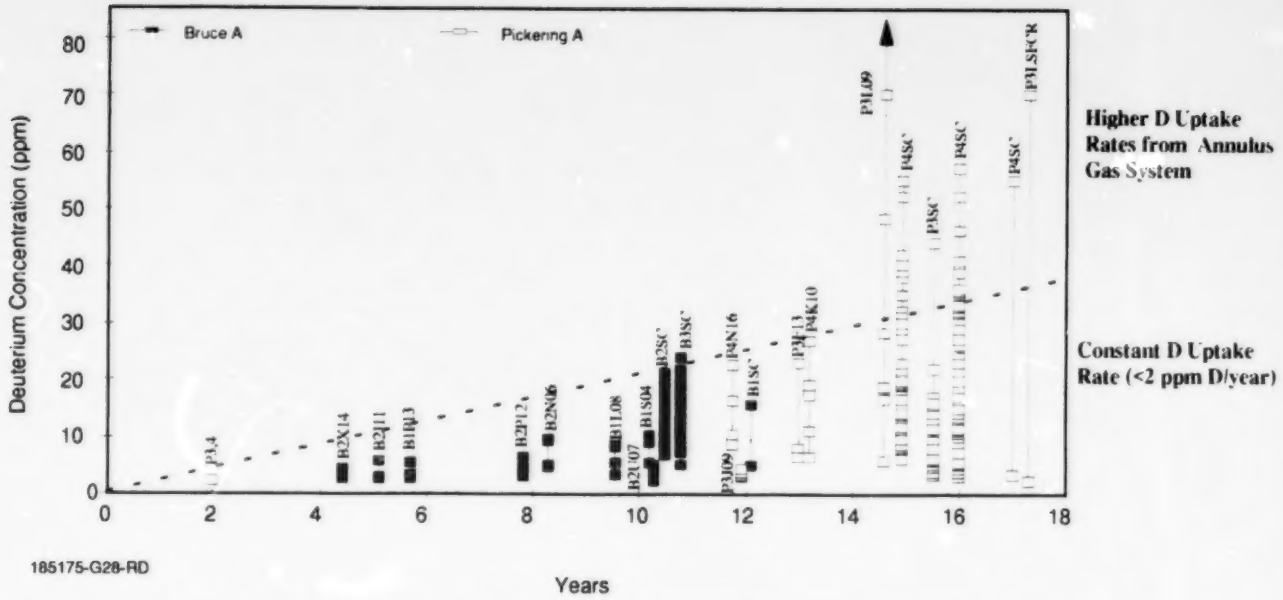

Figure 1 - Deuterium Contents from all Removed/Scraped Pressure Tubes

In pressure tubes for which data is available, deuterium concentrations may be predicted on an individual basis (nominal plus deuterium measurement error of ±12%) assuming a linear increase of deuterium concentration with time. The effective rate of deuterium ingress along the length of the pressure tube is based on the observed exponential relationship between deuterium ingress rate and temperature derived from tube specific deuterium levels and heat transport system temperatures. If deuterium contents are not available, a conservative predicted rate is derived statistically from a sample of pressure tubes with measured deuterium contents. The sample is used to establish a general correlation between ingress rate and temperature. The predicted rate of increase in deuterium concentration for the core population is taken to be the upper bound estimate of the mean rate of the sample for the appropriate temperatures.

We will continue to update the existing data base and analyze data from removed/scraped pressure tubes in 1991, as required.

3.1.2 **Exposure Testing**. The objectives of this program are: to maintain long-term out-reactor aqueous corrosion and hydrogen uptake testing of Zr-2.5 wt% Nb in both the β-quenched and non β-quenched conditions, and Zircaloy-2 pressure tube materials as a function of temperature, and under typical CANDU water chemistry conditions, and also: to develop an understanding of the role of material (impurity content and aging) on corrosion and deuterium uptake in Zr-2.5 wt% Nb. Benefits include providing improved predictive capability for operating reactor pressure tubes, establishing criteria to predict pressure tubes with the highest rates of corrosion and deuterium uptake for inspection and tube removal programs and the development of improved alloys.

Samples of Zr-2.5 wt% Nb and Zircaloy-2 have now been exposed (out of flux) in static autoclaves at 250°C, 310°C and 360°C for exposure duration of up to 1000 days. Zircaloy-2 samples continue to show the lowest weight gains at 250°C and 310°C. Corrosion rates of Zircaloy-2 samples appear to be increasing relative to samples of Zr-2.5 wt% Nb at 360°C, although overall weight gains are similar after 600 days.

Deuterium analyses of a large number of samples have recently been completed. Generally, <5% theoretical uptake is observed in all samples, ie, <5% of the deuterium liberated by the corrosion reaction enters the bulk sample (Figure 2). This is consistent with typical values of percentage theoretical uptake found in removed pressure tubes from Bruce A, indicating that in-reactor exposures do not significantly affect percentage uptake. A few samples show higher percentage theoretical uptakes; reasons for their anomalous behaviour are being investigated.

There is still a general trend towards lower weight gains (corrosion rates) with increased Fe content in samples of Zr-2.5 wt% Nb; this trend is most pronounced at 360°C. Samples with a range of Fe contents which were heat treated (560°C for 24 h) show remarkably uniform corrosion performance, with similar average corrosion rates to those in the as-received condition.

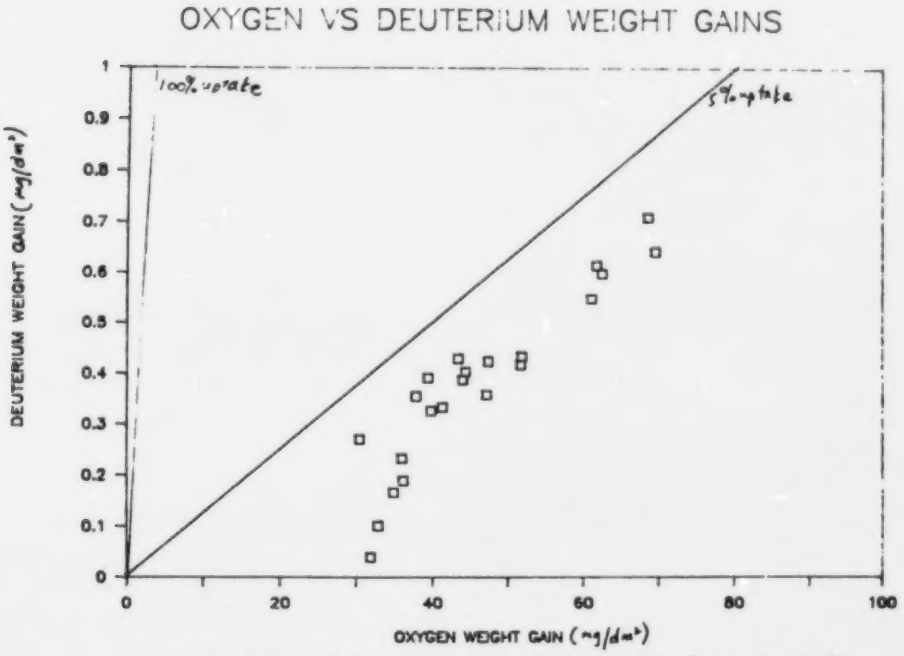

Figure 2 Deuterium vs oxygen weight gain for Zr-2.5 wt% Nb samples (static autoclave, 500 days, aqueous D_2O, pH 10.5, 310°C).

Aqueous autoclave exposures will continue in 1991 at all temperatures extending the total exposure times to 1200 days.

3.1.3 **Mechanisms of Deuterium Ingress**. The objectives of programs in this area are: to characterize near-surface chemical and microstructural changes occurring in pressure tubes following in- and out-reactor aqueous and gaseous exposures, and to develop further understanding of the relationship between oxide structure and composition and rates of deuterium uptake which will improve predictive capability.

3.1.3.1 **Deuterium concentration profiles**. Using Secondary Ion Mass Spectrometry (SIMS) we have obtained deuterium concentration profiles in oxides on samples from the outside surface of removed pressure tubes and those exposed to deuterium gas in the laboratory. These profiles generally show a large drop in the deuterium content from the oxide surface to the metal oxide interface. For example Figure 3 shows typical deuterium concentration profiles in outside surface oxides taken from the outlet region of B1L08. This tube had low bulk alloy deuterium concentrations along its length (<10 ppm w/w D). As shown in this Figure relatively higher deuterium contents were observed in the oxides of samples taken from the hotter 6 o'clock location compared to samples removed from 12 o'clock.

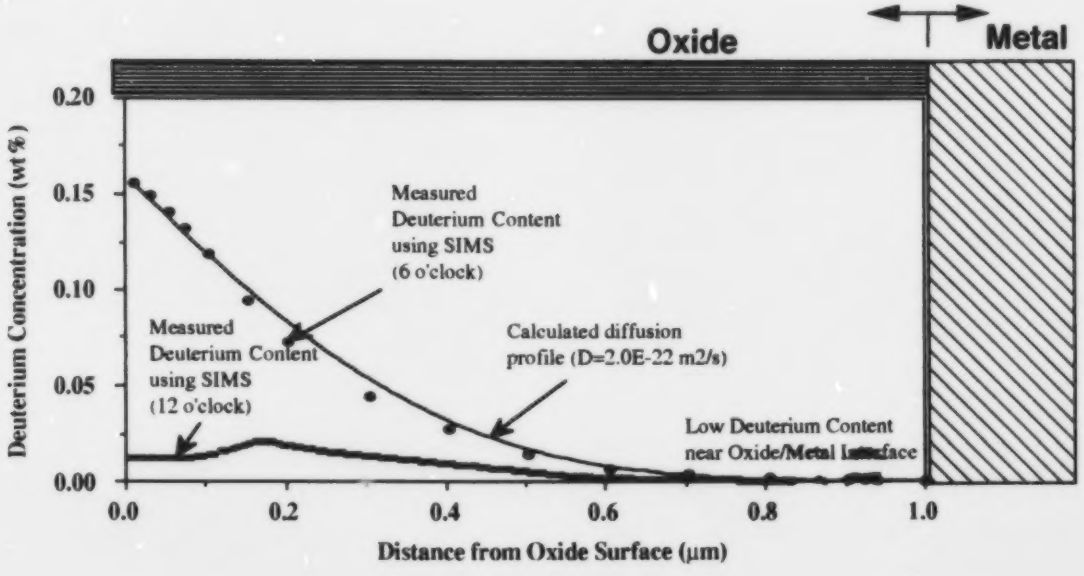

Figure 3 - Through thickness deuterium concentration profiles in outside surface oxides from outlet of B1L08.

In the sample from the 6 o'clock location in Figure 3, deuterium concentration profiles drop very sharply in the oxide to negligible levels at the interface, implying that after 9.5 years in a CO_2 gas annulus at Bruce A, pressure tube outside surface oxides remain excellent permeation barriers to deuterium. The solid line represents the best fit deuterium concentration profile calculated using a diffusion coefficient of 2×10^{-22} m^2/s at 300°C. We have observed similar diffusional profiles in the oxides on samples exposed out-reactor.

3.1.3.2 Oxide structure. The structure of oxides on steam prefilmed Zr-2.5 wt% Nb has been investigated by preparing edge-on foils for examination by transmission electron microscopy (TEM).

Figure 4 shows a schematic of typical oxide structure we have observed to date. The oxide shows a preferred orientation with the base alloy and the columnar grains of oxide (typically 40 nm wide and >200 nm long) are related to the substrate grain orientation. Fine pores were observed throughout the oxide, although the pores were generally small and not interconnected. Discontinuous strips of amorphous material generally ~10 nm thick were observed both at the metal oxide interface and at columnar grain boundaries throughout the oxide.

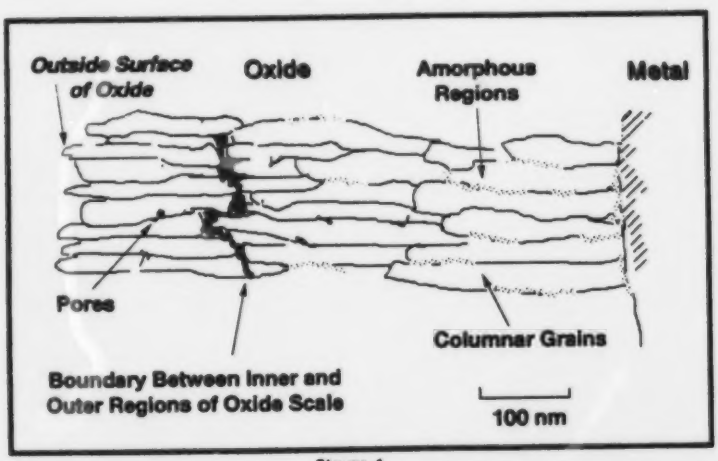

Figure 4

SCHEMATIC OF TYPICAL OXIDE MICROSTRUCTURE ON Zr-2.5 wt% Nb AS-RECEIVED PRESSURE TUBE (From Edge-on Transmission Electron Micrographs)

The presence of such amorphous material may be related to the low value of the effective diffusion coefficient inferred above following both out-reactor and particularly in-reactor exposures of originally steam-prefilmed Zr-2.5 wt% Nb to deuterium-containing gas. Our results show that outside surface oxides on removed pressure tubes remain very effective permeation barriers and that in-reactor exposures may actually improve their performance. Although rates of hydrogen permeation through amorphous ZrO_2 are not known, amorphous

materials in general, particularly SiO_2, are used as permeation barriers. In addition to reducing the rate of deuterium permeation via grain boundaries, the presence of an amorphous oxide structure in interface regions, although discontinuous, may also reduce the total rate of transfer of deuterium from the oxide into the bulk alloy.

Further work is being pursued in 1991 to resolve the critical processes whereby oxides on zirconium alloys may change (improve) their permeability characteristics during exposures in-reactor. Additional TEM studies are therefore, planned. It is also planned to further study the form and distribution of deuterium in oxides, preferred migration routes, and characterize the micro-chemistry of the oxides.

3.2 Heat Exchanger Corrosion

3.2.1 **Program Background**. Heat exchanger (HX) corrosion has cost Ontario Hydro tens of millions of dollars in incapability and equipment replacement costs. The main components affected have been moderator and shutdown HX's. All the failures have been the result of corrosion beneath a layer of fouling on the lake water side of the tubes. The fouling is comprised of inorganic and organic material from the lake water coolant. Alloys N08800, N04400 and AISI type 304 stainless steel have been particularly prone to attack. The mechanisms of corrosion of HX alloys under these conditions is unknown; this makes the selection of methods for alleviating the problem difficult.

Understanding the nature of the corrosion is essential to the efficient control of this form of degradation. Field and laboratory studies have been initiated which are aimed at characterizing the corrosion process(es) and developing mitigation approaches

The 1990 highlights are as follows:

3.2.2 **Field Studies**. The field studies have included the generation of data from model heat exchangers (test rigs) at Darlington and Pickering and tubes (non leaking) removed from operating HX's.

Examination of tube, alloys N08800, N08825 and N08028, removed from the Pickering test rig after three years of exposure to the HX environment exhibited localized corrosion. The N08800 tubes displayed numerous pits. Alloy N08028 and N08825 exhibited pits but only at the hot end of the bundle in the tube sheet region. Pits up to 70% through wall were found in one of the N08028 tubes. Both N08028 and N08825 are currently in service at PNGS-B and DNGS. This observation suggests that leaks due to pitting are likely to occur in moderator HX's at PNGS-B and DNGS in the near future. The examination also revealed important information regarding the preferred location of pitting. The data suggests that attack occurs towards the hot end of the bundle in the vicinity of the baffles i.e. at locations of low flow. These data are important from a design and inspection standpoint.

Moderator HX tubes removed from PNGS-A following eddy current inspection were the subject of a detailed examination. The inspection data had indicated that there were localized defects in the 70:30 copper/nickel alloy tubes; one 90% through wall defect was reported as well as many 50% deep indications. All of the defects indications were found on the lake water side of the tube. The station wanted verification of results because new replacement bundles would have to be ordered immediately if the inspection data was correct. Subsequent examination of four tubes at OHRD indicated that the defects were the result of erosion corrosion. The maximum wall loss observed was 25% of the tube wall thickness; no defects greater than this were found. Based on the results it was reported that the moderator HX's could be operated for another 7 years before they would have to be replaced.

No evidence of the very localized attack found in the N08800, N08028 and N08825 PNGS-B moderator tubes was detected in the PNGS-A 70:30 copper/nickel moderator HX tube.

3.2.3 **Laboratory Studies**. During 1990 most of the laboratory research was directed towards investigating the microbiological aspects of HX corrosion. The development of a method for testing the susceptibility of HX materials to microbiologically influenced corrosion (MIC) has been the main area of research. Attention was focused on the anaerobic sulphate reducing bacteria (SRB), as deposit analysis and corrosion products found in and around pits on moderator tubes were rich in compounds which are associated with these microorganisms.

A collaborative effort between the Biology and the Corrosion and Tritium Technology Sections has concluded that SRB alone are unlikely to be the cause of the problem. The exposure of HX alloys to anaerobic bacteria and electrochemical testing indicated that these microorganisms have an effect on the pitting potential. This observation was verified with electrochemical noise studies which suggested that the presence of anaerobic bacteria inhibits corrosion.

Based on these results it is believed that both anaerobic and aeration conditions are necessary for localized corrosion. The presence of oxygen serves to oxidize HS- to tetrathionate, thiosulphate etc, which are known to cause corrosion of our HX alloys.

3.2.4 **1991 Plans**. The work planned for 1991 comes under four headings:

1. Mechanism Determination
2. Life Predictions
3. Mitigation
4. Monitoring

3.2.4.1 **Mechanism determination**. Mechanism determination will include MIC testing in an environment which involves exposure of samples to combined aerobic and anaerobic conditions. Natural sediments (from moderators) and lake water will be employed for these tests. The type of bacteria to which

the samples will be exposed will be controlled by adjusting the redox potential of the sediment. The tests will be conducted at moderator HX temperatures. Corrosion current and redox potential will be monitored with time. When the coupons have been removed from the test rig they will be examined for indications of corrosion. The number, distribution and depth of corrosion pits will be recorded and corrosion products identified using advanced surface analytic techniques. Silt samples taken from the immediate vicinity of the pits will also be analyzed and bacteria identified and enumerated. The data generated will provide mechanistic information which will help us to select the most resistant HX alloys. Initially, the work will be performed on N08800 and will then be expanded to N08825 and N08028 and candidate replacement alloys.

3.2.4.2 **Life predictions**. Laboratory tests aimed at obtaining pit propagation rates is also planned. The objective of this work is to generate data which can be used by designers and operators to predict the remaining life of HX tubes when pits have been found in them. At present this information is not adequately quantified. A double compartment test cell is proposed for this study. The anode (having a small surface area) and the cathode which has a large surface area are contained in two separate cells which are connected with an agar bridge. The electrolyte contained in the anode cell will contain anaerobic bacteria and the cathode cell will contain aerobic bacteria and or a high pH medium. The anode and cathodes will be shorted and the current flowing between them monitored with time. Charge transfer will be used to calculate pit propagation rates. These experiments will be carried out at 60°C on the current HX alloys (N08800, N08825 and N08028).

The inspection of bundles from the Pickering and Darlington moderator HX rigs will continue during this year and any new information will be reported.

3.2.4.3 **Mitigation**. A program aimed at determining the effect of reagents for removing fouling deposits and treatments for biological control on the localized corrosion of HX alloys is planned. Screening experiments will be carried out in the laboratory. Initially, pitting data will be acquired for non-fouled samples in order to rank the various process media in terms of their aggressiveness towards the test material. The final experiments will consist of exposing fouled tubes to the most and least aggressive cleaning and biological control treatments as previously determined by the pitting tests.

3.2.4.4 **Monitoring**. Work will continue on evaluating corrosion monitoring equipment for systems health monitoring in-plant. The emphasis will be on passive techniques such as electrochemical noise and impedance spectroscopy.

3.3 Corrosion Engineering

The main areas of activity during 1990 were; i) the Lennox cathodic protection installation, ii) the PNGS vacuum building inspection, and iii) the Bruce heavy water plant "D" corrosion survey.

All of the ignition oil piping from the pump house to the Lennox generating plant is cathodically protected per OHRD's specifications. The system is comprised of four self-adjusting rectifiers and continuous polymeric anodes.

The internals of the PNGS vacuum Building were first inspected in 1980, ten years after it had been put in operation. Corrosion of carbon steel and some stainless steel was found to be quite severe in 1980. The second internal corrosion inspection was conducted in 1990. Corrosion was found to be minimal due to better coatings applied in 1980.

Corrosion at the mothballed Bruce Heavy Water Plant was found to be continuing at a low level.

During 1991 the main areas of work are likely to be:

1. Hot water tank corrosion consulting.
2. Preparations for the Bruce vacuum building inspection
3. Zebra mussel induced corrosion (ZIC).

The third of these programs is a new area of research and has been precipitated by the infestation of the Great Lakes with zebra mussels. Mussel attachment to pipes results in blockage and corrosion.

One of the methods of mitigating mussel attachment is the injection of sodium hypochlorite (~2 ppm) into the service water. Unfortunately, this addition can lead to accelerated corrosion of some metallic components (particularly stainless steels). A program is now underway to determine exactly how passivating alloys and carbon steel are affected by the NaOCl treatment. This work is being performed at the Nanticoke test rig. The electrochemical noise technique will be used to monitor the affect of this treatment on the performance of the materials under investigation.

A program aimed at investigating the effectiveness of electrochemical methods of controlling zebra mussels is also planned. Two techniques are currently under consideration; one utilizes a combination aluminium-copper anode and the other a copper anode and sodium hypochlorite. A current is passed through the anodes to release toxins which prevent zebra mussel settlement. Both of these potential control methods are likely to have less of an environmental impact than chlorination.

3.4 Steam Generator Tubing Corrosion

3.4.1 Corrosion Fatigue

Corrosion fatigue cracking has not been an extensive problem for alloy N06600 steam generator tubing; however, the incidence of documented corrosion fatigue failures is rising. Failures due to this mechanism have occurred at:

Oconee, a B&W once-through unit operated by Duke Power Co.,
Ontario Hydro's Bruce NGS 'A',

and more recently at

> North Anna, a Westinghouse unit operated by Virginia Power Co., and Indian Point 3, a Westinghouse unit operated by the Power Authority of the State of New York.

Since a synergistic stress-corrosion/corrosion-fatigue mechanism was believed responsible for the Bruce NGS failures, a project was initiated in 1988 to investigate the high cycle corrosion fatigue behaviour of N06600 and N08800 tubing of CANDU manufacture under conditions relevant to CANDU steam generator operation.

The fatigue response of CANDU N06600 and N08800 tubing is being determined over a range of loading and chemistry conditions encompassing those occurring in service. In order to make efficient use of limited resources, an orthogonal experimental design is employed.

In 1989 development and refinement of the test apparatus was completed and several preliminary fatigue staircases were run. By the end of the year four test frames, each operating independently, were available for the program.

3.4.1.1 1990 review of progress. In 1990 seven fatigue staircases were completed in air and four fatigue staircases were completed in the environmental screening matrix. Two additional staircases, one in air and the other in the environmental matrix, were started.

Testing of U-bend N06600 tubing at 30 Hz for 3.2 million cycles proceeded according to an orthogonal test matrix. Fatigue strengths of about 170 MPa to 240 MPa have been measured with mean stresses of 240 MPa and 300 MPa.

Fatigue testing in aqueous environments is also progressing well. A total of four staircases have been completed in the screening matrix and fatigue strengths of about 160 MPa to 220 MPa have been measured. The results reveal only small environmental effects; fatigue strength in an aqueous environment shows small increases or decreases over those in air for similar test conditions. However, it should be remembered that, for a minimum factorial experiment design, all tests must be completed before analysis of the results is possible.

Also in 1990, finite element analyses were carried out for the stress distribution resulting from applied loads. Two sets of X-ray stress measurements were obtained, providing information about the residual stresses on inside and outside tube surfaces. With all stresses taken into account, measured fatigue strengths compare well.

3.4.1.2 1991 plans. In 1991, the environmental screening test matrix for alloy N06600 will be completed. At that time, the results will be reviewed and plans for a second environmental test matrix will be considered. Testing will begin for alloy N08800 in air and aqueous environments. It is

expected that about one half of the air testing and one third of the environmental testing will be completed in 1991. The remaining tests in the matrix will be carried out in 1992.

Additional stress analyses and residual stress measurements will be obtained for the test specimens. Failed and unfailed test specimens will be examined for location of cracking for comparison with predictions based on stress analysis data.

3.4.2 **Stress Corrosion Cracking**. Stress corrosion cracking of N06600 (alloy 600) tubing has proven to be a major reliability problem in PWR steam generators. Based on this and extrapolation of available research data, it is estimated that cracking of CANDU steam generator material could begin to become a problem after 15 years of operation. Although, only one operational failure of N08800 (alloy 800) has been reported, cracking resistance of this alloy may be less than that of N06600 in certain environments, particularly very strong caustics.

This project was initiated to determine the low temperature stress corrosion cracking resistance of CANDU steam generator tubing alloys N06600 and N08800. To do this, samples of steam generator tubing with simulated process heat treatments are stressed and exposed at steam generator temperatures. Aggressive (high pH) environments are employed to produce results in a reasonable time. The main variable in testing is temperature.

Heat treatment and metallographic assessment of CANDU N06600 tubing was completed in 1987. In 1988 and 1989 a total of about three hundred N06600 and N08800 C-rings were tested in autoclave exposures to 10% NaOH solutions at 290°C and 350°C, with durations of up to 4000 hours. The 350°C testing allowed assessment of the relative cracking resistance of various alloy heat treatment conditions. Very little cracking was observed in 290°C testing.

3.4.2.1 **1990 review of progress**. Autoclave testing proceeded in 1990 under an adjusted test program. Three autoclave tests were started; one at 290°C and two others at 320°C. The first autoclave test at 320°C was completed after 4000 hours. Both remaining tests were extended past their scheduled completion in December, based on the results of the first 320°C test: only short cracks have been found so far in the 4000 hour samples.

A review of electrochemical monitoring for stress corrosion has begun and a sample arrangement has been chosen for preliminary tests. Plans have been made for initial testing in a low-temperature cracking system to acquire some familiarity with the monitoring techniques. This testing has been delayed by unanticipated steam-generator-tube surveillance work for Bruce NGS.

3.4.2.2 **1991 plans**. The adjusted test program will continue in 1991 and will include autoclave testing at 350°C, 320°C and 290°C. The two autoclave tests continued from 1990 will be completed in the first half of 1991. Four autoclave tests are scheduled for start up in 1991; two of these tests will continue into 1992. These will all be very long duration

exposures. The low-temperature cracking tests that were delayed in 1990 will be carried out. It is expected that electrochemical monitoring will prove useful for stress corrosion detection.

3.4.3 **Steam Generator Corrosion Surveillance**. Steam generator performance at Ontario Hydro's nuclear stations has been excellent, with only a few tube failures and a very small number of plugged tubes. However, heavy tubesheet deposits and extensive fouling of support structures has led to a growing concern for the deterioration of steam generator tubing, particularly at Bruce NGS. As fouling increases the likelihood increases of under-deposit corrosion or environmental cracking of the alloy N06600 tubing.

In response to this, tube surveillance, involving eddy current and ultrasonic inspection, and tube removals has been stepped up. In late 1989 and through 1990, seven steam generator tubes were removed from units at Bruce NGS to assess tubing and deposit condition at tubesheets and within U-bends.

3.4.3.1 **1991 review of progress**. In 1990 tubes from both Bruce-A and Bruce-B were examined. These tube examinations have revealed the extent and nature of corrosion degradation, and seem to indicate different corrosion responses at the two stations. Some details of the observations follow.

A tube from Bruce Unit 2 steam generator 6 was examined. Within the sludge pile region, the corrosion product layer was thin and discontinuous; nonuniform general corrosion to a depth of as much as 30 to 40 micrometers was observed throughout this region. Very shallow, <5 micrometers deep, intergranular attack [IGA] was found locally in the tubesheet crevice. There was no apparent corrosion above the sludge pile.

Tubes from Bruce Unit 6 steam generator 6 and Unit 8 steam generator 6 were examined. These tubes were fouled by black magnetite deposits, but there is very little accumulation of sludge on the tubesheets of these steam generators. Shallow non-uniform corrosion and pitting, to a maximum depth of 60 micrometers, has been found beneath the magnetite deposits. The corrosion is not confined to the vicinity of the tubesheet, but extends at least up to the second support plate.

Lakewater and chronic oxygen in-leakage are implicated as major contributors to the corrosion at both stations. Also, it is believed that water treatment plant acid excursions contributed to the degradation. The reason for the different corrosion response at BNGS 'B' versus BNGS 'A' is, at present, unclear.

3.4.3.2 **1991 plans**. It is expected that additional tubes will be removed from units at Bruce NGS in 1991. These tubes will be examined as received and assessed for corrosion degradation. The possible causes and the implications of any observed damage will be considered so that corrective measures can be formulated. Some effort will be expended in 1991 to understand the different corrosion responses at Bruce 'A' and Bruce 'B'.

4. TRITIUM TECHNOLOGY PROGRAM

4.1 Program Objectives

Tritium Technology R&D is focused on supporting a number of corporate groups and activities associated with the handling of tritium. The work effort can be broadly subdivided along three lines: metal getters, tritium metal interactions and gas process handling.

4.2 1990 Program Review

4.2.1 **Metal Getter Program**. The metal getter program can be subdivided into two main thrusts: tritium storage on metal getters and tritium removal from gas streams using metal getters. The tritium storage bed research program is a mature program with current emphasis on the optimization of overall storage bed design, investigation of alternative materials such as zirconium cobalt as a substitute for uranium and design, consulting and testing of tritium storage beds for international tritium facilities in collaboration with CFFTP. Key developments during 1990 in each of these areas are summarized in the following paragraphs.

4.2.1.1 **ZrCo beds**. While uranium remains the preferred material for tritium storage due to its low equilibrium pressure at room temperature, moderate dehydriding temperature, tolerance to trace impurities and minimal influence of helium-3, zirconium cobalt as an alternate storage medium offers some attractive features. The undesirable characteristics of uranium are its pyrophoricity in air at room temperature and the imposed nuclear regulatory controls. ZrCo appears to be less pyrophoric and does not require regulatory controls. Hydriding tests using ZrCo suggest acceptable bed kinetics, alloy stability and tolerance to trace impurities. A bed containing 50 g of zirconium cobalt was designed and tested to study bed heat transport, bed kinetics, conductance and particulate control.

4.2.1.2 **Consulting**. Technical support is provided to CFFTP on an ongoing basis to promote international marketing of storage beds. Tritium storage beds have been designed by OHRD and fabricated with Ontario industry for the University of Rochester Tritium Fill Station and the Kernforschungszentrum Karlsruhe (KfK) Tritium Laboratory in Germany. The two beds for the University of Rochester each containing 100 g of depleted uranium will be used to charge glass spheres for inertial confinement fusion studies. The five beds built for KfK contain 200 g of depleted uranium each and have a capacity to store 3 g of tritium. These units will form the heart of the tritium storage and delivery system at KfK.

4.2.1.3 **Uranium particulate control**. During the loading and unloading process, uranium decrepitates. Under some operating conditions, uranium sintering may also occur. A two year study to determine the operating conditions which may minimize fines production and transmission into the

process loop, has been underway. In this, the second year, a special uranium bed was constructed to measure particulate size directly. This work forms part of a University of Toronto Master's program.

4.2.1.4 **Consequence of air ingress into uranium storage bed**. The consequences of an accidental exposure of a uranium bed to air under a variety of conditions have been studied. Other tests examined responses to nitrogen and to oxygen in argon, helium and nitrogen. Starting temperatures ranged from 21 to 551°C. These tests have been carried out on storage beds containing 5, 25 and 3000 g of uranium powder. Measured quantities included several temperatures, pressures and tritium emission from the 3000 g bed. In every case the temperature excursion resulting from oxidizing and nitriding the uranium powder was modest. Energy balances suggest the UO and UN are the primary reaction products. In every case tritium released from the bed was several orders less than the resident tritium inventory. The hazard associated with an accidental ingress of air into a uranium storage bed is small. The study carried out at Research was a collaborative effort involving Princeton Plasma Physics Laboratory and Idaho Engineering National Laboratory.

4.2.1.5 **Scavenger bed development**. Scavenger beds are devices which preferentially scrub tritium from noble and nitrogen gas streams. Two types of scavenger beds are under development: those which can remove tritium from the effluent stream down to the mCi/m^3 range and those which can purify the stream down to the $\mu Ci/m^3$ range. Uranium is used in the former case while a Zr-Fe alloy is used in the latter case. Both types of beds are being developed for a German nuclear facility. The latter type will also be used at the Research Division tritium laboratory as part of the glovebox cleanup systems. The cross-sectional view of a typical uranium scavenger bed is shown in Figure 5. Gas enters along the central tube, flows to the bottom of the devices and returns to exit by percolating through pie shaped cavities which contain uranium powder. Detritiation factors exceeding 400 can be realized in a single pass. If the uranium is replaced with Zr-Fe alloy detritiation factors exceeding 30,000 have been measured.

4.2.1.6 **Filter plugging**. Uranium particulate is typically in the 0.1 to 4 micron size range. Stainless steel filters within a scavenger bed have a 5 micron rating. A test loop has been assembled to study filter plugging by uranium fines in tritium scavenger beds. The flow loop circulates argon continuously at about 20 L/min through a high flow bed containing 422 g of depleted uranium. To date tests have been conducted using oxidized uranium powder. The pressure drop across the bed suggests that the plugging is not a concern. Similar tests are planned using activated uranium powder.

4.2.2 **Tritium/Metal Interaction Studies**. Activity in the tritium/metal interaction studies' area is subdivided along three fronts: permeation, decontamination of metallic surfaces and utilization of beta energy emitted from a host material.

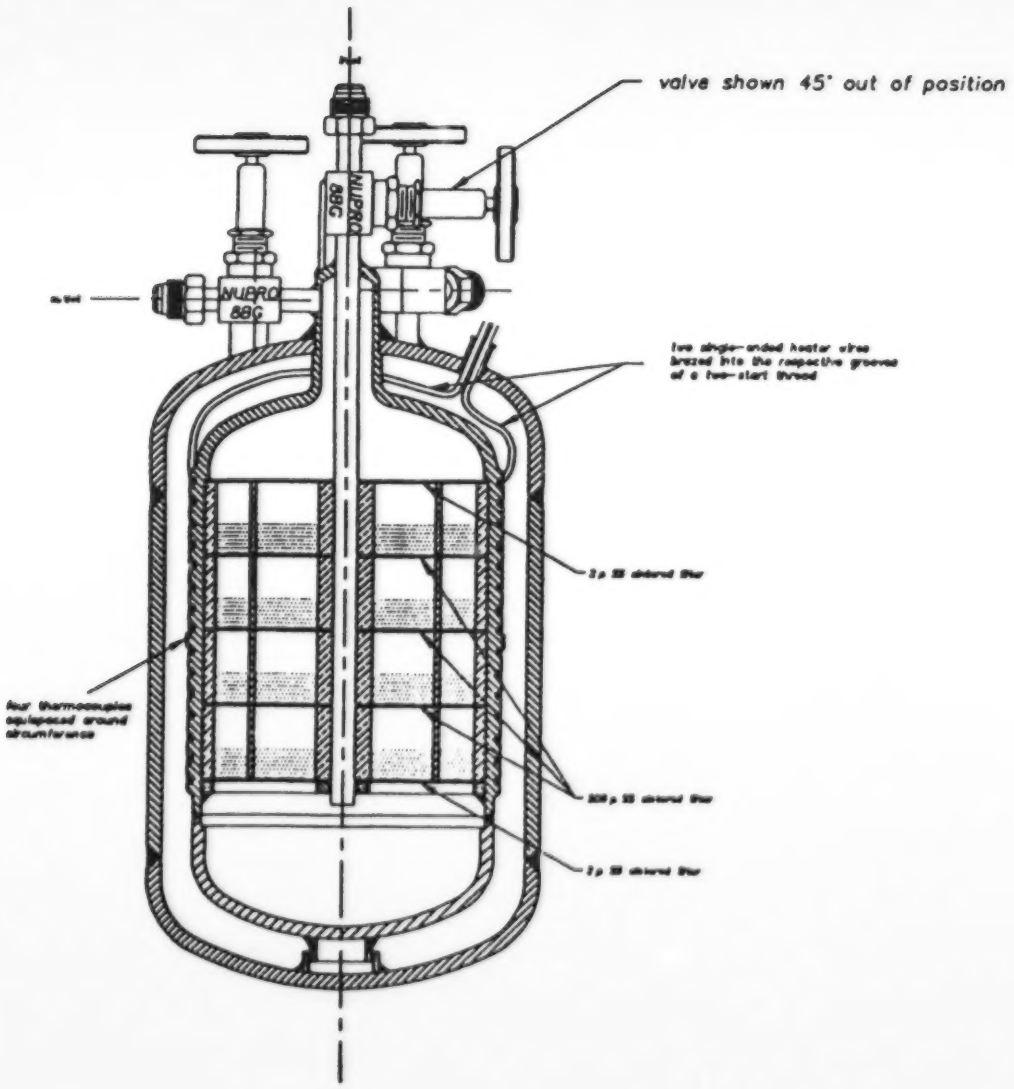

Figure 5 Cross-section of 5 kg Uranium Scavenger Bed

4.2.2.1 **Permeation**. Experiments over the past few years have shown that under special conditions hydrogen can permeate through bimetallic layers at different rates depending on the permeation direction. The metal can be highly transparent to hydrogen in the forward direction and opaque to hydrogen in the reverse direction. This asymmetry in permeation has been exploited in several applications. The focus over the past year has been the development of a hydrogen isotope pump. Hydrogen permeation rates were measured across an iron membrane, under molecular and atomic hydrogen bombardment. Adsorption/desorption of hydrogen on the surfaces controlled the permeation

when molecular hydrogen was incident. When atomic hydrogen was incident on the membrane surface permeation was limited by the bulk properties of iron. The maximum pumping speed measured was 0.05 L/s for the 100 cm^{-2} membrane.

Studies in which a glow discharge was the source of atomic hydrogen were also carried out. In this case, the electron temperature was in the range of 2.3 to 5.2 eV, energies typically found in a fluorescent light with atomic fluxes in the range of 10^{18} to 10^{23} H°/m^2s striking the membrane surface. The plasma ionization fraction varied from 10^{-6} to 10^{-3}. The incident atomic flux varied linearly with the current density as long as significant gas heating did not occur. Atomic fluxes produced by the glow discharge can produce large atomic hydrogen fluxes. However, materials with higher permeabilities that are required in high throughput pumps are to be developed.

4.2.2.2 **Decontamination**. Metal components which have been in contact with tritium gas will outgas tritium bearing species and are the progeny of additional tritium surface contamination within the lab. Routine decontamination of tools and components is essential if surface activity within the lab or at the TRF is to be controlled. Exposure of contaminated components to a low energy plasma offers one potential method for routine decontamination. A decontamination system consisting of a reaction chamber and an insitu measurement system has been built and is operational. The tritiated items are placed in the reaction chamber and exposed to a low pressure plasma. Effluent is removed from the chamber by vacuum pumps and sent to a bubbler detection system. Both HT and HTO in the effluent stream are measured. The performance of the decontamination facility has been studied for a range of discharge operating conditions and gases: hydrogen helium, argon and hydrogen/argon mixtures. It appears that tritiated metallic surfaces can be rapidly decontaminated to nonactive levels using this approach.

4.2.2.3 **Tritium powered lights**. Gas tubes coated with a scintillant and filled with tritium have been used as light sources. These devices have been proposed for runway lighting in remote locations. However, they are vulnerable to breakage. An alternative scheme which uses tritium locked in thin titanium films and intimately mated with scintillant, is being developed. Several solid tritium lights based on titanium tritide were constructed and examined for their light outputs against identical light sources powered by tritium gas. This permitted a direct comparison of the two tritium power sources, while factoring out geometrical and phosphor differences. The solid lights examined included titanium tritide films in contact with a thin film CaS(Ce) phosphor, ZnS(Cu) and ZnO powder phosphor coatings; and, titanium tritide powder mixed with ZnS(Cu) phosphor powder and glass microspheres in various proportions. Generally, in each instance it was observed that the titanium tritide solid light output was about one-third of the equivalent tritium gas powered light, which is in accord with the predictions of theoretical calculations. Factors predicted by the model which permit enhanced light output are being tested.

4.2.3 **Gas Handling/Equipment Development**. Work programs in this area are embodied in the development and operation of the tritium laboratory. Five gloveboxes in the tritium laboratory have been commissioned. Nitrogen gas, delivered from a liquid nitrogen tank, is used in each box. ZrFe scavenger beds remove tritium from the box cover gas and the vacuum effluent streams. Tritium monitors, designed at Research routinely survey the tritium concentration leaving each box to the stack. Each box is supported by an airlock air exchange system. These systems permit the passage of items into and out of the glovebox without entraining air into the box or tritium from the box into the lab. Six airlock pumpout systems have been built and commissioned in the past year. A preliminary design of the Secondary Enclosure (SEC) System has been completed. All key components have been ordered and received. Special components designed at OHRD and fabricated by Ontario industry are in the final stages of production. Several international facilities have expressed interest in purchasing both types of systems. Plans to market these systems are in preparation by CFFTP.

A turbomolecular pump modified by Leybold Heraeus for tritium service has been under evaluation at OHRD over the past two years. A bearing failure in the pump following two months of tritium testing has stopped testing. The failure was not related to the tritium exposure. After decontamination of the pump by flushing with argon and baking at 100°C, the pump was dismantled in preparation for component replacement. Replacement of the pump bearings, rotor assembly, and the resistance temperature detectors is now underway at OHRD. The oil lubricated steel bearings will be replaced with grease lubricated ceramic bearings before testing resumes. Research will assist Darlington personnel to balance turbomolecular pumps which have failed at the TRF.

4.3 1991 Research Plans

Several experimental thrusts are proposed for the year 1991. These have been subdivided into four major categories: DNGS support, tritium interaction with metals, tritium laboratory support and metal getter studies. The main activities and the rationale for these activities are described within each subdivision.

4.3.1 **Research Program in Support of DNGS**. Several tasks in support of the Tritium Removal Facility at DNGS are proposed for 1991. These are: development of a decontamination center, improvement to the assay system of the Tritium Immobilization System (TIS) and consulting support during the design of the TRF Annex.

4.3.1.1 **Development of a decontamination center**. While the results of metal decontamination using a low pressure plasma are very encouraging, and suggest that the majority of the surface contamination can be removed within a few minutes, it is too early to implement a facility in the field. Several questions must be resolved. Which gas provides the best decontamination results. What is the operating pressure range; higher is better from a

facility design point of view. How can the contamination of the chamber be minimized? What is the regrowth rate of tritium activity? Can inner surfaces be decontaminated also?

4.3.1.2 **Improvements to the assay system of TIS**. A review of the PVT assay technique is required to ensure that errors associated with the measurement of each aliquot of tritium stored are below 1%. This uncertainty translates into 450 curies per batch! This task proposes to review the current practice for determining the amount of tritium sent to storage and to quantify the error associated with each measurement necessary to compute that amount. RGA analysis is used to determine the gas species leaving the cryogenic columns. Measurements taken by DNGS personnel and analyzed at OHRD suggest that the tritium impurity content can be measured to at least 0.5% without any corrections. A task to confirm the measurement accuracy of the quadrupole system using an RGA and a GC system at Research is proposed. Additionally, a new development in leaks through pin holes suggest that the intermediate expansion volume currently used in the TIS may be unnecessary. Tests are required to confirm that the operating range is valid for TRF operation. A leak may offer an attractive simplification in the assay procedure.

4.3.1.3 **Consulting in support of the TRF annex**. A cursory review of the drawings for the proposed Annex at the TRF reveals a lack of tritium relevant equipment or active gas handling facilities. The tritium laboratory at OHRD has been operational for approximately three years. Concepts implemented at OHRD are also applicable to the TRF Annex. A consulting role by OHRD in support of designing the Annex is proposed.

4.3.1.4 **Turbomolecular pump decontamination and balancing**. A Leybold Heraeus turbomolecular pump modified for tritium service is under evaluation at OHRD. The bearings have recently been replaced and the rotor needs balancing. Steps are underway to train a technician in the balancing of turbomolecular pumps with equipment available locally. Two turbomolecular pumps which have seen service at the TRF, also need balancing. A task which involved training the TRF technicians to balance the TRF pumps at OHRD is proposed.

4.3.2 **Tritium Interaction with Metals**. Research activity in this area has increased significantly in the past two years and is expected to become a dominant area over the next few years. Several clients support a broad range of studies: CFFTP, Darlington and Health and Safety Division.

4.3.2.1 **Decontamination**. Surfaces which have been exposed to tritium can pose a health hazard in several ways: directly, through the inhalation of tritiated volatiles which outgas from a surface, or the exposure of personnel by contact with a surface and indirectly through the spread of tritium to uncontaminated surfaces and the subsequent contact with personnel. A three pronged program is proposed for 1991 to address the following questions:

1. What species desorb from stainless steel? What fraction is water?

2. Is outgassing from surfaces contaminated at DNGS similar to that from a clean surface exposed to pure tritium gas?

3. Is rf decontamination an attractive alternative to washing?

The tritiated species which outgas from stainless steel will be measured by two experiments: a Linear Thermal Desorption (LTD) experiment using a nitrogen sweep gas to carry the species to a bubbler system and an LTD experiment in which the desorbing species are monitored using a radio frequency mass spectrometer in vacuum. Preliminary tests using both facilities suggest that the majority of the tritium released is HTO as is evident in Figure 6. However, the possibility of another component which is collected by the same bubbler as HTO and which may contribute significantly to uptake in workers has not been excluded.

4.3.2.2 Low water retention surfaces. Tritium gas strives to equilibrate with the surfaces it wets, even if the exposure time is short. Two undesirable side effects result: the tritium gas is converted to HTO and the HTO desorption occurs over a prolonged period. This effect has been indirectly observed in the OHRD Tritium Laboratory stack. If the surfaces can outgas in the work environment, they will represent a low level chronic emission source. Surface treatments which can render stainless steel hydrophobic would be attractive for tritium gas service minimizing both chronic HTO release and reducing the outgassing time. The proposed program will investigate surface treatments of stainless steel which can reduce water retention and measure the change in water retention relative to stainless steel using tritium as the water tracer. To this end a stainless steel surface will be exposed to a low tritium concentration in air and the recovery of background conditions will be monitored for a range of tritium concentrations, exposure times and surface treatments.

4.3.3 Tritium Laboratory Support Programs. Efforts continue to reduce tritium emission from the tritium laboratory and to automate the routine activities within the laboratory. Two key objectives have been identified for the current year: the installation and commissioning of a computerized data acquisition system and the development of a secondary enclosure cleanup system.

4.3.3.1 Computerized data acquisition system. Several key elements within the tritium laboratory require routine monitoring and recording. These include the stack flow rate, tritium concentration in the effluent, tritium concentration within the laboratory and several parameters associated with gloveboxes. A central data collection and processing network is planned based on Hewlett Packard components. This work will be headed by a scientist on attachment from the research facility CNR located in Milan, Italy.

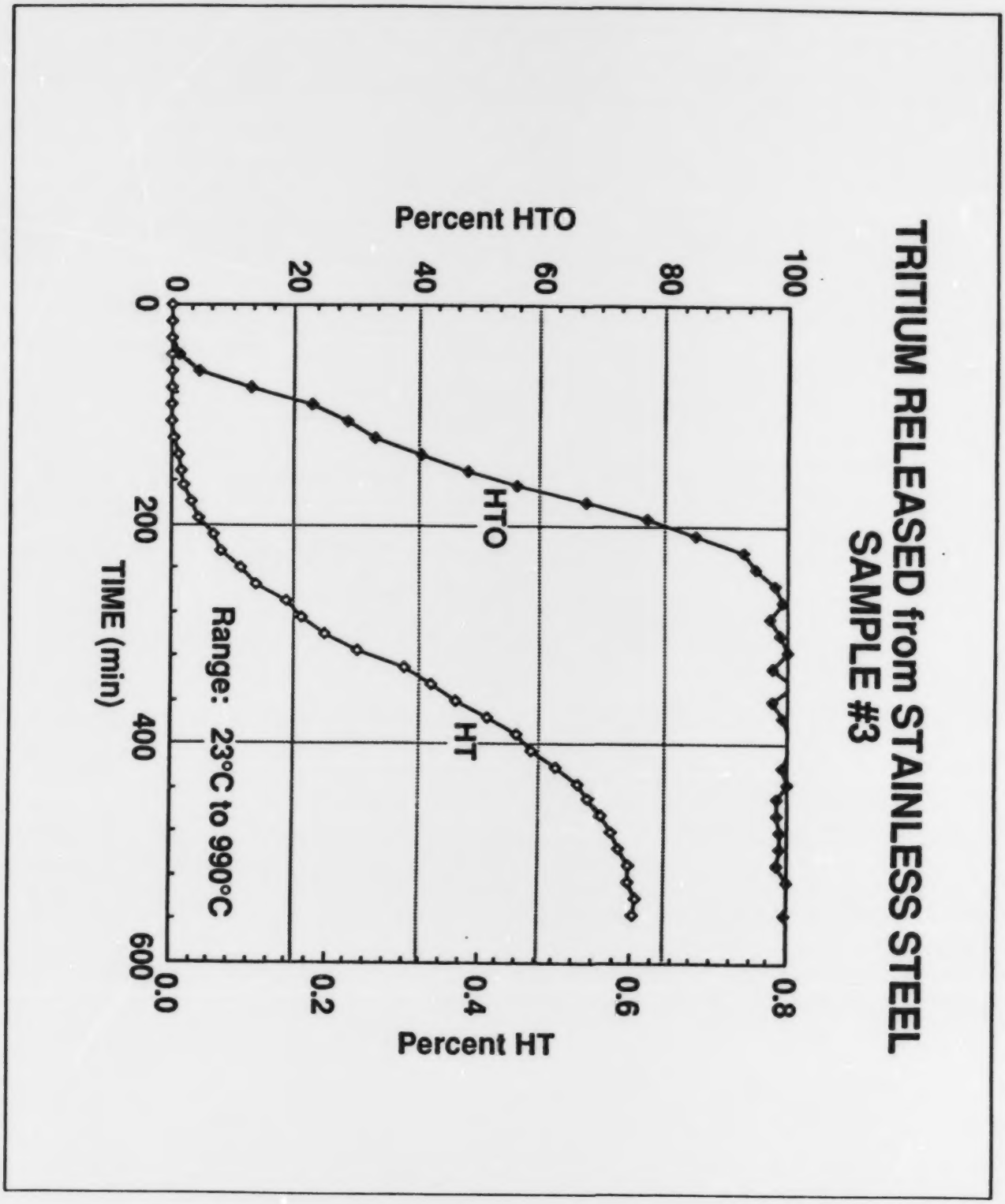

Figure 6: Tritium Released from Stainless Steel (Sample #3)

4.3.3.2 **SEC system development**. The Secondary Enclosure Cleanup (SEC) system, under development at Research Division for three years, is intended to remove tritium which has been released into a glovebox atmosphere. Several tasks are outstanding. The system tritium monitors need to be tested. Heat exchangers need to be designed and fabricated. The pressure controller system needs to be constructed and tested. The flow diagram and the P&I diagram for the system need to be finalized. A control panel complete with logic circuitry needs to be developed. A comprehensive review to assess the consequence of failure of components is required to ensure most credible off normal conditions are anticipated and addressed. To this end, two engineers will be attached to OHRD and dedicated to this effort: one from CFFTP and one from SAES Getters, Milan, Italy. The objective of their stay will be to review and complete the overall design of the SEC system, to test a prototypic system, to install the system on a glovebox and to test its performance.

4.3.4 **Metal Getter Studies**

4.3.4.1 **Scavenger evaluation program**. Zirconium based alloys have been pressed into service during the past three years to remove tritium at trace levels: that is to say, in the parts per billion to the parts per million range, from noble and nitrogen gas streams. Several applications have emerged. However, a systematic study of the performance of these materials has not been undertaken. A program which permits their evaluation for flow rates ranging from a few litres per minutes to 0.6 L/s with concentrations as high as 100 kCi/m^3 and in the presence of contaminants at ppm levels is planned. This program is expected to span three years. Specific objectives for 1991 are: to measure the purification factor of ST198 at flow rates in the range of 10 to 40 L/m and for inlet concentrations up to 100 kCi/m^3. Also, to determine the optimal unloading procedures, to measure the residual tritium inventory on the scavenger and its impact on bed performance, to measure the purification factor of ST198 for three species: T_2, HTO, CH_4 for a range of inlet concentrations and bed operating temperatures and to generalize the performance of scavenger beds for extrapolation to a range of sizes.

4.3.4.2 **Aging effects of ZrCo and ST737**. Zirconium cobalt, ZrCo, has been proposed as a tritium storage medium in the NET Tritium Storage and Delivery System and is under consideration as an alternative to uranium in several laboratories. A significant fraction of the helium-3 which is produced during the radioactive decay of tritium, can be trapped within the lattice structure. The induced stresses may dramatically alter the equilibrium dissociation pressure and the rate at which tritium can be loaded on ZrCo. A study to measure the degradation of the equilibrium dissociation pressure of tritium over ZrCo and changes in the pumping speed of the material as a function of time is proposed.

The dynamic and equilibrium properties of ST737 have been studied during 1990 as part of a collaboration with scientists from CNR, Milan, Italy. The results suggest that this material may also find utility in tritium storage and delivery systems provided tritium within the matrix of ST737 does not

significantly alter the virgin properties. The thrust of the current task is to investigate the change in alloy properties, if any, as a consequence of exposure to tritium. This work is similar to the ZrCo aging studies proposed above.

5. ACKNOWLEDGMENTS

The progress described in this report is the result of the continuing dedicated and hard work of all members of the section. The work program is large and each individual has been involved in maintaining our longer term core research program, while at the same time contributing to many shorter term, but equally high priority projects. These individual contributions are gratefully acknowledged.

Approved by:

J. Brown
Manager
Metallurgical Research Dept.

PCL:km

Prepared by:

P.C. Lichtenberger
Supervising Scientist
Corrosion & Tritium Technology Section
Metallurgical Research Department

TABLE 1

CORROSION AND TRITIUM TECHNOLOGY
STAFF AS OF YEAR END 1990

Dr. P.C. Lichtenberger	(Phil)	Supervising Scientist
Mrs. K.A. Mile	(Kim)	Section Assistant

a) Corrosion Group

Dr. B.D. Warr	(Brian)	Scientist
Mr. P.J. King	(Peter)	Engineer
Mr. A.M. Brennenstuhl	(Alex)	Scientist
Dr. K.W. Lam	(Kim)	Engineer
Dr. G.I. Ogundele	(Gabriel)	Engineer (temporary)
Dr. M.B. Elmoselhi	(Mohammad)	Engineer (temporary)
Mr. A.C. Headon	(Al)	Senior Technologist
Mr. J.W. Mummenhoff	(Juergen)	Technologist
Mr. E.M. Rasile	(Elvio)	Technologist
Mr. S.W. Borda	(Steve)	Technician
Mr. L. Grant	(Laniel)	Technician
Ms. B. Guest	(Bonnie)	Technician
Mr. L. Chee	(Lloyd)	Technician
Mr. J. DeLuca	(Jerry)	Technician

b) Tritium Technology Group

Dr. W.T. Shmayda	(Walter)	Unit Head - Tritium Technology
Mr. A.G. Heics	(Andy)	Engineer
Mr. N.P. Kherani	(Nazir)	Scientist
Dr. A.B. Antoniazzi	(Armando)	Scientist
Mr. K.D. Geiger	(Ken)	Technologist
Mr. B.L. Fishbein	(Bernie)	Technologist
Mr. R.J. Opatril	(Rad)	Technologist
Mr. M.D. Hooper	(Mark)	Technician

CONFERENCE/SEMINARS ATTENDED
VISITS TO OUTSIDE ORGANIZATIONS
CORROSION AND TRITIUM TECHNOLOGY SECTION

DATE	AUTHORS	DESCRIPTION
February 27-March 1	P.C. Lichtenberger	Steam Generator Reliability Project Technical Advisor Group Meeting, Charleston, S.C.
March 26-28	B.D. Warr	Microscopy of Oxidation, Cambridge, England
April 11	M.B. Elmoselhi P.C. Lichtenberger	Microstructural studies in support of COG Research Programs, CRNL
April 30-May 3	A.M. Brennenstuhl P.J. King G.I. Ogundele P.C. Lichtenberger	Steam Generator and Heat Exchanger Conference - Canadian Nuclear Society, Toronto, Ontario
May 15	W.T. Shmayda	SAES Getters, Milan, Italy
May 16	W.T. Shmayda	Institute for Plasma Physics, CNR, Milan, Italy
May 17	W.T. Shmayda	ISPRA Establishment, Ispra, Italy
May 22	W.T. Shmayda	Radium Chemie, Teufen, Switzerland
May 23-24	W.T. Shmayda	KfK Karlsruhe, Germany
May 25	B.D. Warr M.B. Elmoselhi	Surface Science Western at the University of Western Ontario, London, Ontario
May 28-31	N.P. Kherani	Lasers for the 90's: Course/symposium on advances in lasers and applications, University of Toronto, Physics Department
June 5	W.T. Shmayda P.C. Lichtenberger	TFTR, Princeton University, New, Jersey, USA
June 14	B.D. Warr M.B. Elmoselhi	Meeting on corrosion & hydrogen ingress in Zr alloys, CRNL
June 25-28	P.C. Lichtenberger	EPRI S/G TAG Meeting, Philadelphia, PA
June 27	M.B. Elmoselhi	"Surface Engineering: Current Trends and Future Prospects", University of Toronto
July 9	B.D. Warr M.B. Elmoselhi	Visit to Nuclear Physics Department, Queens University

Sept 3-7	M.B. Elmoselhi B.D. Warr N.P. Kherani	Int'l Symposium on Metal Hydrogen Systems - Banff, Alberta
Sept 25-26	N.P. Kherani	Radioluminescent Light Technology Transfer Conference - Annapolis, Maryland
Sept 28-29	N.P. Kherani	Ontario Centre for Materials Research, Alliston, Ontario
October 8-11	N.P. Kherani	American Vacuum Society
October 7-11	A.G. Heics	9th Topical Meeting on the Technology of Fusion Energy Oak Brook, Illinois
October 8-11	N.P. Kherani	American Vacuum Society, Toronto, Ontario -Sputter Deposition and Ton Beam Processes -Surface Preparation for Thin Film Deposition -Mechanical Properties of Thin Films.
October 8-12	A.B. Antoniazzi	American Vacuum Society, Toronto, Ontario
October 8-12	M.B. Elmoselhi	American Vacuum Society, Toronto, Ontario
October 8-12	P.C. Lichtenberger	American Vacuum Society, Toronto, Ontario
October 23-25	P.C. Lichtenberger	EPRI SGRP TAG Meeting, Palo Alto, CA
October 24	N.P. Kherani	MacWorld Exposition, Toronto, Ontario
November 5-8	B.D. Warr	ASTM Conference, Kobe Japan, "Zirconium in the Nuclear Industry"
November	B.D. Warr	EPRI-NFIR Meeting, Pittsburgh, PA
November 8	W.T. Shmayda	University of Toronto-Ph.D. Oral for M. Galley

PRESENTATIONS/PUBLICATIONS
CORROSION AND TRITIUM TECHNOLOGY SECTION

DATE	AUTHORS	DESCRIPTION
March 26	B.D. Warr E. Rasile M.B. Elmoselhi	Microscopical and Compositional Analyses of Oxides in Zr-2.5 wt% Nb Following In- and Out-Reactor Exposures; Institute of Metals Conference, London, England
April 11	B.D. Warr M.B. Elmoselhi	TEM & SEM Analyses of In-Reactor and Out-Reactor Oxides on Zr-2.5 wt% Nb Pressure Tubes, CRNL Microstructural Studies Meeting
April 30	A.M. Brennenstuhl P.J. King	The Corrosion of Freshwater Cooled Nuclear Heat Exchangers at Ontario Hydro, Steam Generator and Heat Exchanger Conference, Toronto, Ontario
May 7-8	W.T. Shmayda N.P. Kherani A. Heics K. Geiger	CFFTP Advanced Tritium Safe Handling Course
May 6	P.J. King C.D. Litke K.W. Lam	The Corrosion Behaviour of Copper Nuclear Fuel Waste Containers, 92nd CIM Meeting
May 15	W.T. Shmayda	Theory of Getter Storage Beds, SAES Getters, Milan, Italy
May 17	W.T. Shmayda	Tritium Technology at OHRD ISPRA Establishment, Ispra, Italy
June 5	W.T. Shmayda	Pyrophoricity of Uranium Storage Beds TFTR, Princeton University, New Jersey
June 6	W.T. Shmayda	Getter Technology for T_2 Service, Canadian Nuclear Society, Toronto
June 18	P.C. Lichtenberger P. Spekkens	Ontario Hydro S/G R&D, presented to EPRI SGRP TAG, Philadelphia, PA
June 27	P.C. Lichtenberger	Hydrogen Ingress into Zr-Nb Pressure Tubes - An Update, presented to the AECB, Toronto, Ontario
June	A.M. Brennenstuhl B.D. Warr	Three Dimensional SIMS In-Depth Profiling of Protium and Deuterium in Zr-Nb Alloy and its Surface Oxide. 38th ASMS Conference on Mass Spectrometry and Allied Topics

September	M.B. Elmoselhi	Kinetics of Hydrogen Uptake by Zr-2.5 wt% Nb; Effect of Temperature - Proceeding of Int'l Symposium on Metal-Hydrogen Systems
September	N.P. Kherani W.T. Shmayda	Electron Flux at the Surface of Titanium Tritide Films - Proceeding of Int'l Symp on Metal Hydrogen Systems, J. of the Less Common Metals
October 8	A.M. Brennenstuhl, P.E. Doherty T. Dunstall, and P.J. King	The Effects of Biofouling on the Corrosion of Nickel HX Alloys at Ontario Hydro, Int. Congress on MIC, October 1990, Knoxville, TN
October 8	A.M. Brennenstuhl/P. Doherty	The Economic Impact of Microbiologically Influenced Corrosion at Ontario Hydro's Nuclear Power Plants, Int. Congress on MIC, October 1990, Knoxville, TN
October 10	M.B. Elmoselhi, B.D. Warr and N.S. McIntyre	Diffusion as a Rate-Limiting Step in the Transport of Hydrogen Across Thin Oxides of Z-2.5 wt% Nb Presented as a poster at the 37th Annual Symposium of the American Vacuum Society - Toronto, Oct 8-12, 1990
October 10	A.G. Heics, W.T. Shmayda and N.P. Kherani	Zirconium Cobalt for Tritium Storage:Some Bed Design and Operation Considerations, Presented at the 9th Topical Meeting on the Technology of Fusion Energy, Oak Brook, Illinois
October 12	P.C. Lichtenberger	Corrosion & Tritium Technology Outline of Section Program to Queens University Materials Science Students
October 30	P.C. Lichtenberger	AGS Hydrogen Ingress Review of Understanding for D&D, CPSD, COG, Toronto, Ontario
November 5-8	B.D. Warr, M.B. Elmoselhi, A.M. Brennenstuhl, P.C. Lichtenberger, N.S. McIntyre S.B. Newcomb	Oxide Characteristics and their Relationship to Hydrogen Uptake in Zirconium Alloys, 9th International Symposium on Zirconium in the Nuclear Industry, Kobe, Japan.
November 5-8	B.D. Warr, D.O. Northwood and X. Meng	Microstructure of Zr-2.5 wt% Nb Alloy Pressure Tubing, 9th International Symposium on Zirconium in the Nuclear Industry, Kobe, Japan.

December	B.D. Warr, A.M. Brennenstuhl, N.S. McIntyre, C.G. Weisener, R.D. Davidson, W.N. Lennard, G.R. Massoumi and I. Mitchell	Analysis of Zr-Nb Pressure Tube Surfaces for Hydrogen Using Secondary Ion Mass Spectrometry (SIMS), Surface and Interface Analysis, Vol. 15, 591-597, (1990)
November	B.D. Warr, A.M. Brennenstuhl N.S. McIntyre, C.G. Weisener and R.D. Davidson	Deuterium In-Depth Analysis of Oxidized Zr-Nb Pressure Tube Samples Removed from an Operating Nuclear Reactor, Proc. 7th Int. Conf. on SIMS (SIMS VII), Benninghove, A.R. et al, eds. Wiley (Chichester, U.K.) pp 723-726 (1990)
December 3	A.G. Heics	Zirconium Cobalt for Tritium Storage, Presented at the CFFTP 3rd Annual Cdn Meeting on T2 Technology, Toronto, Ontario
December 3	W.T. Shmayda	Decontamination of Stainless Steel Results of Air Ingress Experiments, 3rd Annual Cdn Meeting on T2 Technology, Toronto, Ontario
December 6	W.T. Shmayda/N.P. Kherani	Status of Thin Film Experiments, Toronto, Ontario

VISITORS TO RESEARCH DIVISION
CORROSION AND TRITIUM TECHNOLOGY SECTION

DATE	CONTACT	VISITOR/ORGANIZATION	PURPOSE
January	A.G. Heics W.T. Shmayda	R. Mahoney - High Vacuum Systems Inc.	Getter bed conditioning and testing - technology transfer to industry.
February 1-2	A.G. Heics W.T. Shmayda	E. Rathjen - Kernforschungszentrum (KfK)-Gmbh	Testing of 200 g uranium tritide beds for KfK.
February 5	W.T. Shmayda	C. Phillips, University of Toronto, Chemical Department	Uranium particulate sizing studies.
February 28	W.T. Shmayda	G. Longhurst, Idaho National Engineering Laboratory, Idaho Falls, Idaho	Uranium storage bed safety.
April 12	A.G. Heics N.P. Kherani	Frans Moons & Amie Bruggeman, Nuclear Research Centre, Belgium	Tritium technology programs.
June 7	A.G. Heics	Dr. L. Rodrigo, AECL-CRNL	Tritium technology programs.
August 30-31	W.T. Shmayda N.P. Kherani	H. Albrecht, KfK, Karlsruhe, Germany	Visiting hydrogen and tritium laboratories. Discuss areas of mutual interest and collaboration.
September 24	P.J. King	COG WP19 Members	Inspection of fretted tubes from a Bruce Unit 6 steam generator.
October 1	W.T. Shmayda	Dr. F. Ghezzi, National Research Institute for Plasma Physics, Milan, Italy	Participate in evaluation of ST737 alloys for tritium storage.
October 15	W.T. Shmayda	Dr. Uda Mitsui, Matsugu, Giego, Tritium Processing Lab, JAERI, Japan	Tritium Technology Review
October 22-26	W.T. Shmayda	Dr. Rossmassler, Princeton, University, New Jersey	Participate in air ingress into uranium storage bed study.

REPORTS ISSUED
CORROSION & TRITIUM TECHNOLOGY SECTION

DATE	CAT	REPORT #	FILE NO AND JOB NO	TITLE AND AUTHORS
Feb 20	B	M90-3-K	827.4 82-246-4531	"1989 Corrosion Inspection at the Mothballed Bruce Heavy Water Plant-D", A.C. Headon
March 13	B	M90-14-K	827.411 82-246-4531	"LIMA Evaluation at Heriot-Watt University, Edinburgh", A.M. Brennenstuhl
March 19	X	X90-16-R	125-RPAC	"Program 52 Champions Nuclear Generation Out-Reactor Components", J.A. Chadha, P. Spekkens, and P.C. Lichtenberger
March 27	B	M90-12-K	827.22 82-505-50452	"Analyses of Pits Found on a Sanicro 28 Tube Removed from the Pickering Heat Exchanger Rig", A.M. Brennenstuhl
June 26	B	M90-28-K	827.32 82-078-018	"Evaluation of Corrosion in Lambton TGS Unit 2 LP Heater Drains", G.I. Ogundele
June 26	B	M90-41-K	827.31 82-068-026	"Evaluation of Fireside Corrosion on Boiler Tubes Lambton TGS, Unit No. 2", G.I. Ogundele
July 24	A	89-211-K	827.24 82-139-40161	"Corrosion of Copper as a Used Nuclear Fuel Disposal Container Material: Effects of Sulphide Ions and γ Radiolysis", K.W. Lam
August 3	A	90-115-K	827.48 82-112-552	"Detailed Analysis of Tubes Removed From the Pickering NGS Model Heat Exchanger Rig After Various Exposures Times", A.M. Brennenstuhl
August 8	B	M90-38-K	827.231 82-112-552	"Pressure Tube End Plug Analysis", A.M. Brennenstuhl
August 29	B	M90-61-H	827.2 82-127-553	"Corrosion Survey of Non 285.5 Metallic Components Within the Pickering NGS 'A' and 'B' Pressure Relief Duct, May 1990", A.C. Headon
August 30	B	M90-65-K	827.31 82-202-570	"Materials Performance in Pre-Boiler Systems During Thermal Plant Lay-Up - A Literature Review", G.I. Ogundele
Sept 6	B	M90-62-H	827.21 82-127-553	"Corrosion Survey of Non 285.5 Metallic Components Within the Pickering NGS Vacuum Building, May 1990", "A.C. Headon
Sept 21	B	M90-67-K	827.31 82-078-016	"Waterside Corrosion - A Compilation of Results on Boiler Tube Failure Analysis", G.I. Ogundele

Oct 18	A	89-199-K	827.28 82-500-653	"Zr_2Fe Tritium Scavenger Beds", N.P. Kherani
Dec 5	B	M90-75-K	823.413 81-082-028	"Evaluation of Corrosion in Lennox TGS Auxiliary Boiler #2", G.I. Ogundele
Dec 10	B	M90-70-K	827.22 82-115-504	"BNGS-A Primary Storage Fuel Bay Heat Exchanger Examination", A.M. Brennenstuhl
Dec 14	B	M90-83-K	827.21 82-520-052	"Examination of Steam Generator Tubes from Water Lancing Qualification Trials", P.J. King